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## POROUS CERAMIC FILM AND ITS PRODUCTION

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### Abstract of JP9157062

**PROBLEM TO BE SOLVED:** To provide ceramic filters having various compositions, each of which is provided with one-dimensional through-pores low in pressure drop and is appropriately used for separating molecules or fine particles.

**SOLUTION:** This ceramic film is provided with one-dimensional through-pores each of which extends from one surface of the film to the other and has a pore size of a few nanometers, and produced on a substrate made of glass, a ceramic material, plastic material or heat-resistant metal by forming a composite film consisting of a ceramic phase and a metallic phase with a vapor growth method and then, removing the metallic phase in the composite film with an etching method. Thus, the objective porous ceramic film provided with one-dimensional through-pores each having a pore size of the order of a few nanometers can be synthesized with good reproducibility. Also, by forming such ceramic films on various substrates, ceramic filters each of which shows an excellent function capable of separating molecules or fine particles each having a size of a few nanometers can be manufactured.

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CLAIMS

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[Claim(s)]

[Claim 1] Porous-ceramics film which is porous-ceramics film which has the pore of the nano meter size which penetrates the metal phase in the bipolar membrane which consists of a ceramic phase which formed membranes by vapor growth, and a metal phase in single dimension on another front face from one [ which is removed and obtained ] membranous front face, and is characterized by forming the porous-ceramics film concerned on the substrate of glass, the ceramics, plastics, or a heat-resistant metal.

[Claim 2] Porous-ceramics film according to claim 1 which is a compound more than a kind as which said porous-ceramics film is chosen from a metallic oxide, metallic carbide, and a metal boride.

[Claim 3] Porous-ceramics film according to claim 1 or 2 whose substrate which supports said porous-ceramics film is a porous body.

[Claim 4] Porous-ceramics film according to claim 1 whose average aperture of said pore penetrated in single dimension is 5-100 nanometers.

[Claim 5] The manufacture approach of the porous-ceramics film of having the pore of the nano meter size penetrated in single dimension on another front face from one front face of the film characterized by forming on a substrate the bipolar membrane which consists of a ceramic phase and a metal phase, and subsequently removing the metal phase in bipolar membrane by etching by vapor growth.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the porous-ceramics film and its manufacture approach. In more detail, this invention relates to the approach of manufacturing the porous-ceramics film and the porous-ceramics film concerned of various presentations which have the single dimension penetration pore with little pressure loss used suitably with sufficient repeatability, in order to separate a molecule and a particle. The porous-ceramics film of this invention is useful as a separation means of the molecule of various kinds [ discover / the isolation in nano meter size ], or a particle etc.

**[0002]**

**[Description of the Prior Art]** The ceramic filter excellent in thermal resistance and corrosion resistance aiming at separating the molecule contained in hot gas or a corrosive liquid and a particle is developed. As an approach of producing a porous-ceramics object or the porous-ceramics film, ceramic raw material fine particles are sintered and many methods of using the open pore (free passage pore which carries out opening to the front face of a ceramic object) formed in the process in which a ceramic object carries out eburnation as it is are adopted (JP,7-8729,A). However, by the ceramic object which carried out in this way and was produced, or the ceramic film, there was a problem that it was difficult to arrange the size of pore size, and it difficult to produce the pore of nanometer order with sufficient repeatability.

**[0003]** Although the porosity silica is produced by the technique of having considered as the attempt which produces the porous body which has the pore size to which nanometer order was equal with sufficient repeatability, and having combined a sol-gel method and spinodal decomposition (Nakanishi et al., "Ceramic Transactions and Porous Materials", The American Ceramics Society, and 51-60 (1992)), the organization where the silica phase was connected in the shape of a mesh in this case is formed, the configuration of pore is irregular, and that direction is random.

**[0004]** Thus, since many ceramic parts into which the configurations of pore are scattered on in the molecule and particle which move in the filtration direction that it is irregular and the direction is non-orientation, and bar migration existed, there was a problem which pressure loss generates.

**[0005]** In order to solve the above-mentioned problem, development of the ceramic film which has the pore (it may be hereafter called single dimension penetration pore) which pore size is nano meter size and moreover penetrates in single dimension is tried. As the typical example, there is porosity alumina film by anodic oxidation of aluminum (JP,6-37291,B). Pore size can control the film produced by anodic oxidation of aluminum by the production condition in several nm to dozens of nm, and since a membranous presentation is an alumina, it has the advantage that considerable thermal resistance and corrosion resistance are expectable. However, in the case of the porosity alumina film by anodic oxidation, there is a fault that it is restricted to the alumina of amorphism with the film stable only near ordinary temperature obtained, and only an aluminum plate can be chosen from the constraint on the principle of using anodic oxidation in the electrolytic solution of an aluminum plate with metal aluminium foil or thickness, as a substrate.

**[0006]** As the approach of compensating the fault of the porosity alumina film by the above-mentioned anodic oxidation, the approach of imprinting a pore pattern to a polymer membrane is tried, using as mold the porosity alumina film produced by anodic oxidation (Masuda et al.; Ceramic Society of Japan, 1995 spring annual convention drafts, p485 3F4 01). However, there is a fault that it is difficult to stick the membrane which the ingredient which

imprints the structure of the porosity alumina film by anodic oxidation in this case is restricted to the organic substance, and imprinted membrane structure on other substrates, and to consider as new bipolar membrane.

[0007]

[Problem(s) to be Solved by the Invention] The purpose of this invention cancels the above-mentioned fault which the conventional technique has, and is to offer the porous-ceramics film which has the single dimension penetration pore of available nano meter size in a gas separation membrane or a catalyst with various ceramic ingredients (a metallic oxide, metallic carbide, or metal boride). Furthermore, it is in offering the new bipolar membrane in which various kinds of porous-ceramics film was formed on the substrate of the substantia compacta or porosity which consists of glass, the ceramics, plastics, or a heat-resistant metal, and offering the approach of manufacturing such ceramic film with sufficient repeatability.

[0008]

[Means for Solving the Problem] It is the porous-ceramics film which has the pore of the nano meter size penetrated in single dimension on another front face from one membranous front face which this invention is made that the aforementioned technical problem should be solved, and the porous-ceramics film of this invention removes the metal phase in the bipolar membrane which consists of a ceramic phase which formed membranes by vapor growth, and a metal phase, and is obtained, and is characterized by to form the porous-ceramics film concerned on the substrate of glass, the ceramics, plastics, or a heat-resistant metal. The desirable porous-ceramics film by this invention is at least one kind of compound with which the matter which constitutes the aforementioned porous-ceramics film was chosen from a metallic oxide, metallic carbide, and a metal boride. The substrate with which other desirable porous-ceramics film of this invention supports said porous-ceramics film is a porous body. The average aperture of said pore penetrated in single dimension of other desirable porous-ceramics film of this invention is 5-100 nanometers. The manufacture approach of the porous-ceramics film of this invention is characterized by forming on a substrate the bipolar membrane which consists of a ceramic phase and a metal phase, and subsequently removing the metal phase in bipolar membrane by etching by vapor growth.

[0009]

[Embodiment of the Invention] Then, this invention is further explained to a detail. That is, the porous-ceramics film of this invention is produced in two steps of processes. On a first stage story, the film on which the metal and the ceramic ingredient (a metallic oxide, metallic carbide, or metal boride) were intermingled on the nano meter scale using vapor growth, such as a spatter, is produced. At this time, the detailed organization for which the ceramic ingredient enclosed the surroundings of the metal phase which grew in the shape of a column is formed by controlling the mixing ratio and membrane formation conditions of the metal phase and ceramic ingredient to be used ( drawing 1 ). In this invention, it is possible to change an aperture with the particle size of a metal phase. In this case, the mean particle diameter of a metal phase is changeable in about 5-500nm with the volume fraction and membrane formation conditions of a metal phase and a ceramic phase (substrate temperature, residual-gas pressure at the time of a spatter, etc.). Moreover, the thickness of the grain boundary phase which remains as a ceramic filter part can be changed with the volume fraction of a metal phase and a ceramic phase. Therefore, it is possible to change a film presentation and membrane formation conditions independently as a parameter in the case of producing the film, and the thickness of an average of a grain boundary phase can be changed by about about 1-50nm. SiO<sub>2</sub> to which the part which looks dark in drawing 1 is Co crystal grain, and the part of the shape of a white mesh deposited in the grain boundary of Co crystal grain It is a part. The mean particle diameter of Co crystal grain is about 12nm and SiO<sub>2</sub>. The width of face of a grain boundary layer is about 2nm. Membrane structure similar to this is a Co-Pt system alloy and SiO<sub>2</sub> with the magnetic film of a hard magnetic disk. It has realized by mixed stock (Japanese Patent Application No. No. 51410 [ seven to J]). Then, the porous-ceramics film which finally has the penetration pore of a single dimension is obtained by removing a metal part using an acid or alkali on a second stage story. The schematic diagram of the procedure which forms the porous-ceramics film of this invention on a porous-ceramics substrate is shown in drawing 2 . The situation that (a) formed the sectional view of a porous-ceramics substrate on the ceramic substrate among drawing, and (b) formed the metal membrane (the pore on the front face of a substrate is filled up with a metal), As for (c), the condition which ground the front face, the condition in which the metal and ceramic bipolar membrane of this invention were formed on the film with which (d) was obtained by (c), and the condition after (e) is eluted in a metal by etching by the acid are shown, respectively until a ceramic substrate front face appears.

[0010] As vapor growth used on a first stage story, although a spatter, vacuum deposition, a CVD method, the laser

ablation method, or a molecular beam epitaxy method can be considered, it is desirable to use a spatter in consideration of mass-production nature or the possibility of large area membrane formation.

[0011] As a combination of a metal and a ceramic ingredient, a metal and a ceramic ingredient should just be the combination which starts phase separation at the time of membrane formation. The metal or the alloy which is the metal which is easy to grow in the shape of a column as a metal phase, and dissolves easily in an acid and alkali and which binding energy with oxygen, carbon, and boron is easy to return to it small in order to use the ceramic phase which deposited into the grain boundary part of the metal phase which grew in the shape of a column for the pore part after etching the metal phase which grows in the shape of a column in this invention as a residual phase is desirable. More than a kind chosen from the alloy which makes a principal component alkaline earth metal, such as an alloy and Mg, and it which make a principal component 3d transition metals, such as V, Cr, Mn, nickel, Fe, Co, Cu, and Zn, and them in consideration of the ease of the handling at the time of a spatter practical is suitable. In addition, aluminum, In, Sn, Pb, etc. are available. As a ceramic phase used as a residual phase, more than a kind chosen from borides, such as carbide, such as oxide, such as an alumina, a mullite, cordierite, a spinel, a zeolite, and forsterite, silicon carbide, titanium carbide, and zirconium carbide, titanium boride, zirconium boride, and boron carbide, can use suitably.

[0012] When forming the bipolar membrane of the above-mentioned metal and the ceramics by a spatter etc., on a metaled target, the wafer of ceramic ingredients, such as a metallic oxide, metallic carbide, and a metal boride, can be placed, and it can use as a multicomponent target. Still more preferably, in order to make small dispersion in a presentation inside the film after membrane formation, the composite material mixed to homogeneity by the powder metallurgy-approach at the time of target production is prepared.

[0013] The substrate used in case the above porous-ceramics film is manufactured can be chosen from glass, the ceramics, plastics, and a heat-resistant metal, and can also use not a still more precise substrate but a porous substrate. As a heat-resistant metal used for a substrate, oxidation-resistant alloys, such as stainless steel which consists of Fe, nickel, Cr, V, etc., and Hastelloy, are suitable. Drawing 2 shows how to form membranes, using a porous-ceramics substrate as an example. That is, the front face is ground in the condition of having sunk a metal or resin into the front face of the ceramic porous body of dozens of micron meter from the several nm average aperture, and a smooth front face is formed. Subsequently, this front face is washed using water, a surfactant, an organic solvent, etc., and the spatter film is formed on it by making this into a substrate. At this time, it is desirable to use what is removed on the etching conditions same as the metal which sinks in, or resin as the ingredient of the above-mentioned metal target.

[0014] Next, with an acid or an alkali solution, etching processing is carried out and the metal component in the obtained bipolar membrane is removed. It is desirable to choose suitably according to the class of metal which can use a sulfuric acid, a hydrochloric acid, a nitric acid, oxalic acid, an acetic acid, etc., and should be carried out elution as an acid used by this etching processing. Since the ceramic part formed of the first membrane formation process has many amorphous or things which have low extent of crystallization, it is desirable to etch on weak etching conditions using the fully diluted solution. For example, Co is used as a metal component and it is SiO<sub>2</sub> as a ceramic component. When using, it is desirable to process with the etch rate of 0.3nm/s using the nitric-acid water solution of 0.003 conventions.

[0015] As stated above, in case the manufacture approach of the porous-ceramics film of this invention forms the porous-ceramics film, it produces the bipolar membrane of a metal and the ceramics by vapor growth, it is characterized by using combining the approach etching subsequently removes a metal phase, and can offer the various porous-ceramics film which has new structure and a new presentation. As for the porous-ceramics film of this invention, it is possible to make the isolation in nano meter size discover, and it is useful as a filter for separating a molecule and a particle etc. The porous-ceramics film of this invention can control independently the width of face of pore size and a grain boundary phase (thicken width of face of a grain boundary phase especially), and essentially differs from the conventional anodic oxidation alumina film etc. at this point.

[0016]

[Function] When the two phase from which the chemical durability which consists of a metal and ceramics (a metallic oxide, a metal boride, metallic carbide) differs by the forming-membranes methods, such as a spatter, in this invention forms the bipolar membrane intermingled with nanometer order, subsequently removes only a metal part by acid etching etc. and makes a ceramic part remain, it becomes possible to compound the porous-ceramics film which has single dimension penetration pore with little pressure loss. That is, by controlling membrane formation conditions appropriately, the metal phase which is one of the main membrane components is grown up in the shape of a column, a ceramic ingredient is deposited in the grain boundary, and it becomes possible by removing a metal phase by etching

further to obtain the porous-ceramics film which has the single dimension penetration pore of the pore size of nanometer order.

[0017] Moreover, in order to form the bipolar membrane before carrying out acid etching by a spatter etc., it becomes available [ the thing of a variety and various ingredients, such as a metal, glass, ceramics, and plastics, and a gestalt ] at the substrate which supports the film.

[0018]

[Example] An example explains this invention concretely below.

They are metals Co and SiO<sub>2</sub> on a soda lime glass substrate with an example 1 thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO<sub>2</sub> of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO<sub>2</sub> so that 20% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might serve as 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither substrate heating nor impression of bias voltage was performed at the time of membrane formation.

[0019] The structure of the compound thin film which formed membranes is shown in the transmission electron microscope photograph of drawing 1 . Drawing 1 is the enlargement which carried out grinding of the glass substrate, removed it, carried out ion polish of the bipolar membrane further, made thin, and was seen from the direction perpendicular to a film surface. With this photograph, Co crystal grain child with a mean particle diameter of 12nm is growing in the shape of a column, and it is SiO<sub>2</sub> amorphously to a grain boundary. It deposits.

[0020] Next, it was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness produced by the above-mentioned approach for 5 minutes, and dissolution removal of the Co phase was carried out. Drawing 3 is the enlargement which observed the film after carrying out dissolution removal of this Co phase with the scanning electron microscope. Co phase is eluted nearly completely and it is SiO<sub>2</sub> of a grain boundary. It remained in the shape of a mesh. Expansion of the ceramic film obtained by drawing 4 by doing in this way and an example of a perspective view are shown.

[0021] By the same procedure as example 2 example 1, they are metals Co and SiO<sub>2</sub> on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO<sub>2</sub> of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO<sub>2</sub> so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0022] Drawing 1 is resembled very well, the crystal grain child of Co grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO<sub>2</sub> amorphous to that grain boundary. It deposited and the mean particle diameter of Co crystal was large a little with about 20nm in this case. It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO<sub>2</sub> of a grain boundary. It remained in the shape of a mesh.

[0023] By the same procedure as example 3 example 1, they are metals Co and SiO<sub>2</sub> on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO<sub>2</sub> of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO<sub>2</sub> so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and heated the substrate at about 200 degrees C at the time of membrane formation.

[0024] Drawing 1 is resembled very well, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO<sub>2</sub> amorphous to that grain boundary. It deposited and it turned out [ about 35nm and ] that the mean particle diameter of Co crystal is still larger in this case.



[0025] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO<sub>2</sub> of a grain boundary. It remained in the shape of a mesh.

[0026] By the same procedure as example 4 example 1, they are metals Co and SiO<sub>2</sub> on the Hastelloy substrate with a thickness of 2mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO<sub>2</sub> of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO<sub>2</sub> so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0027] It is very well alike in drawing 1, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO<sub>2</sub> amorphous to that grain boundary. It deposited and the mean particle diameter of Co crystal in this case was about 25nm.

[0028] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO<sub>2</sub> of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from the Hastelloy substrate were not accepted.

[0029] In the same procedure as example 5 example 1, the compound thin film which consists of two phases of metals Co and SiO<sub>2</sub> was formed on the alumina substrate with a thickness of 5mm. In a spatter, it is SiO<sub>2</sub> of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO<sub>2</sub> so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rate at this time is about 1 nm/sec, and neither heating of a substrate, nor impression of bias voltage was performed at the time of membrane formation.

[0030] It is very well alike in drawing 1, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO<sub>2</sub> amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 19nm.

[0031] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO<sub>2</sub> of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from an alumina substrate were not accepted.

[0032] By the same procedure as example 6 example 1, they are metals Co and SiO<sub>2</sub> on a polyethylene film substrate with a thickness of 0.8mm. The compound thin film which consists of two phases was formed. In a spatter, it is SiO<sub>2</sub> of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO<sub>2</sub> so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. The membrane formation rates at this time are about 0.8 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0033] It is very well alike in drawing 1, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is SiO<sub>2</sub> amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 26nm.

[0034] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO<sub>2</sub> of a grain boundary. It remained in the shape of a mesh. When a polyethylene film was used as a substrate, exfoliation of the film took place quite notably in process of the etching processing by the acid. However, when the front face of a polyethylene film was processed by corona discharge treatment or the silane coupling agent before forming bipolar membrane by the spatter, it turned out that exfoliation is pressed down considerably.

[0035] The metal Co with a thickness of 100nm was formed on the porosity silica substrate with a thickness of 2mm by example 7 spatter. The front face of the substrate after membrane formation was ground with diamond polish equipment, it left Co got blocked in the pore of a silica, Co phase on a substrate was removed, and the smooth polished surface was acquired. They are metals Co and SiO<sub>2</sub> on this substrate. The compound thin film which consists of two phases was formed. In a spatter, it is SiO<sub>2</sub> of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the glass tip was used. At this time, it is SiO<sub>2</sub> so that 10% of the total surface area of one side of a target may be occupied. The amount of a glass chip was adjusted. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.8 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0036] It is very well alike in drawing 1, Co crystal grain child grows in the shape of a column, and the structure of the thin film which formed membranes is SiO<sub>2</sub> amorphous to the grain boundary. It deposited and the mean particle diameter of Co crystal was about 26nm.

[0037] Co phase which was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of this thickness for 5 minutes, and was got blocked in the pore of a silica, and Co-SiO<sub>2</sub> formed on it Dissolution removal of the Co phase in bipolar membrane was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is SiO<sub>2</sub> of a grain boundary. It is \*\*\*\*\* to be removed nearly completely [ Co phase which remained in the shape of a mesh and was got blocked in the pore of a porosity silica substrate ]. Moreover, most exfoliations of the bipolar membrane from a porosity silica substrate were not accepted.

[0038] In the same procedure as example 8 example 1, the compound thin film which consists of two phases of Metals Co and SiC was formed on the soda lime glass substrate with a thickness of 1.2mm. The multicomponent target which placed the SiC sintered compact tip of 1cm angle on the metal Co target with a diameter of 6 inches was used for the spatter. At this time, the amount of a SiC sintered compact chip was adjusted so that 20% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.9 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0039] The structure of the compound thin film which formed membranes was very well alike in drawing 1, Co crystal grain child grew in the shape of a column, and the phase considered to be amorphous SiC by the grain boundary deposited. This Co crystal grain child's mean particle diameter was about 35nm.

[0040] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase was eluted nearly completely and SiC of a grain boundary remained in the shape of a mesh.

[0041] By the same procedure as example 9 example 1, they are metals Co and ZrB<sub>2</sub> on a soda lime glass substrate with a thickness of 1.2mm. The compound thin film which consists of two phases was formed. In a spatter, it is ZrB<sub>2</sub> of 1cm angle on a metal Co target with a diameter of 6 inches. The multicomponent target which placed the ceramic tip was used. At this time, it is ZrB<sub>2</sub> so that 20% of the total surface area of one side of a target may be occupied. The amount of a ceramic chip was adjusted. After exhausting a vacuum tub to 5x10<sup>-6</sup>Torr, Ar gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2x10<sup>-2</sup>Torr, the RF of 600W was inputted, and the plasma was generated. Membrane formation rates are about 0.9 nm/sec, and neither heating of a substrate nor impression of bias voltage was performed at the time of membrane formation.

[0042] It is very well alike in drawing 1, Co crystal grain child grows in the shape of a column, and the structure of the compound thin film which formed membranes is ZrB<sub>2</sub> amorphous to that grain boundary. It deposited and this Co crystal grain child's mean particle diameter was about 21nm.

[0043] It was immersed in the nitric-acid water solution of 0.003 conventions of the bipolar membrane of 50nm of thickness for 5 minutes, and dissolution removal of the Co phase was carried out. Like the case of an example 1, Co phase is eluted nearly completely and it is ZrB<sub>2</sub> of a grain boundary. It remained in the shape of a mesh, and most exfoliations of the film from a soda lime glass substrate were not accepted.

[0044]

[Effect of the Invention] As explained in full detail above, it is the porous-ceramics film which has the pore of the nano

meter size penetrated in single dimension on another front face from one membranous front face, this invention relates to the porous-ceramics film characterized by forming the porous-ceramics film on the substrate of glass, the ceramics, plastics, or a heat-resistant metal, and its manufacture approach, and according to this invention, it can offer the porous-ceramics film which has a single dimension through tube with little pressure loss. Moreover, the porous-ceramics film of this invention can be used as a ceramic filter, if it combines with a porous-ceramics substrate. And since the quality of the material of this ceramic filter can be broadly chosen from a metallic oxide, metallic carbide, a metal boride, etc., it can use properly as it chooses the high-melting quality of the materials, such as metallic carbide and a metal boride, when the high thermal resistance near 2000 degree C is required, and it chooses a metallic oxide, in using it in a hot oxidizing atmosphere. Moreover, if the porous-ceramics film of this invention is produced by the spatter and etching, the porous-ceramics film can be formed at a substrate ingredient on the substrate of almost all ingredients, such as organic materials, such as other plastics of a metal, glass, and the ceramics. Moreover, when forming bipolar membrane by the spatter, it is also possible to form membranes to homogeneity on the substrate of the large area which can form membranes even if the shape of surface type of a substrate is not flat, and amounts to several square meters.

[0045] The ceramic filter which combined the porous-ceramics film and porous-ceramics film of this invention with the porous-ceramics substrate is applicable to removal of the harmful particle contained in general works exhaust air, the exhaust gas of a thermal power station, and the exhaust gas of an automobile etc., if it controls [ for the purpose of pore size ] only as a mere gas separation membrane. Moreover, it can be used for separation of the very fine particle-like matter in a liquid, for example, a very minute microorganism like a virus, the separation of a colloid molecule ensemble distributed in the solvent, sieving of a specific molecule, etc.

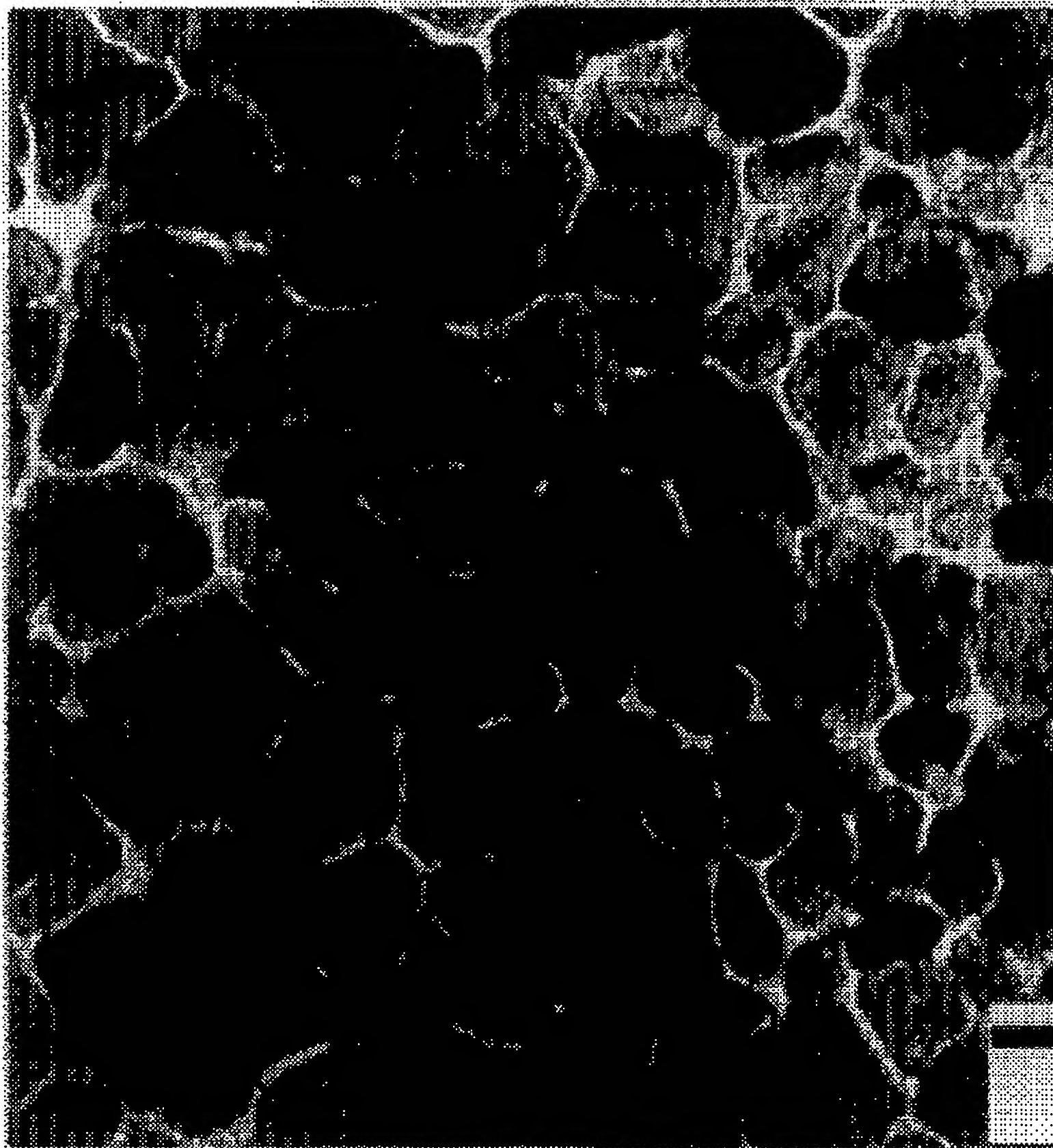
[0046] Furthermore, if the front face of membranous penetration pore is embellished with an inorganic or organic catalyst, it is possible to obtain the catalyst film with more high activity.

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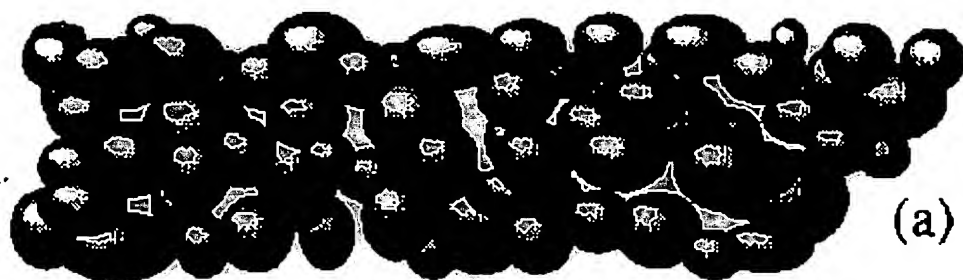
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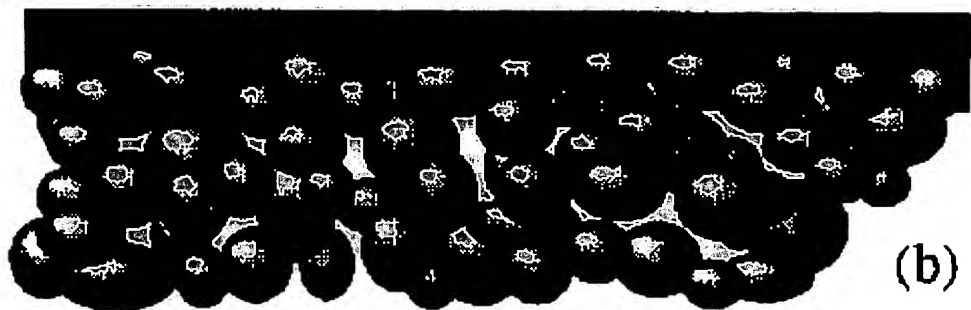
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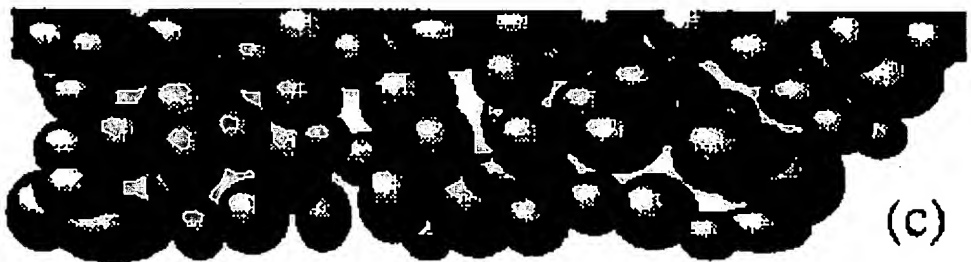
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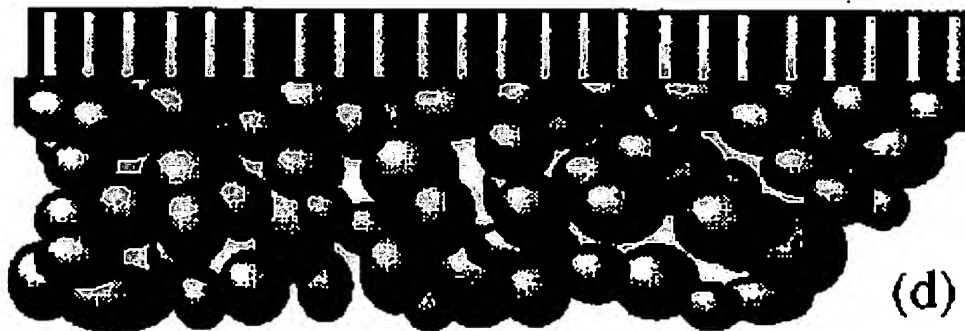
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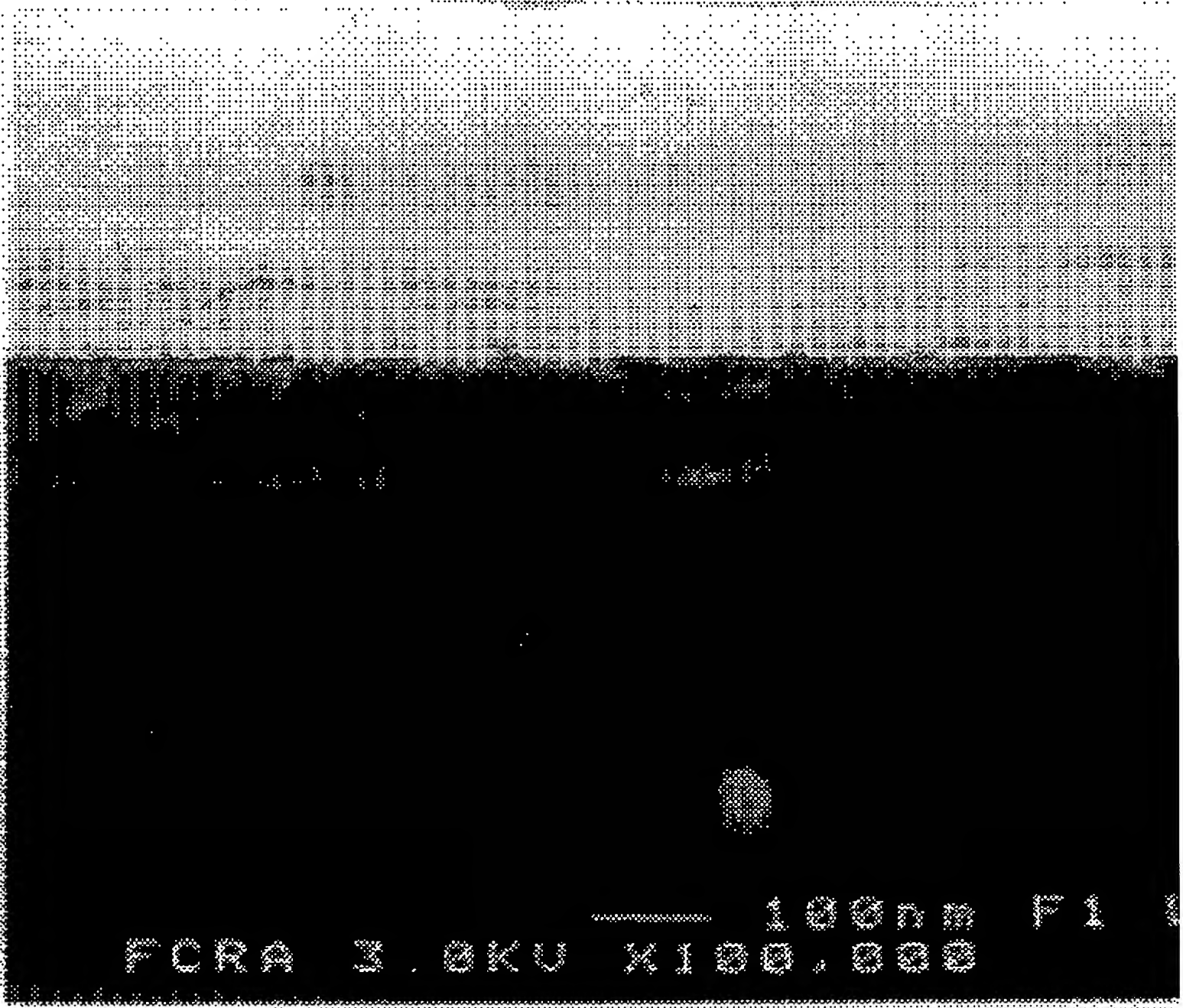


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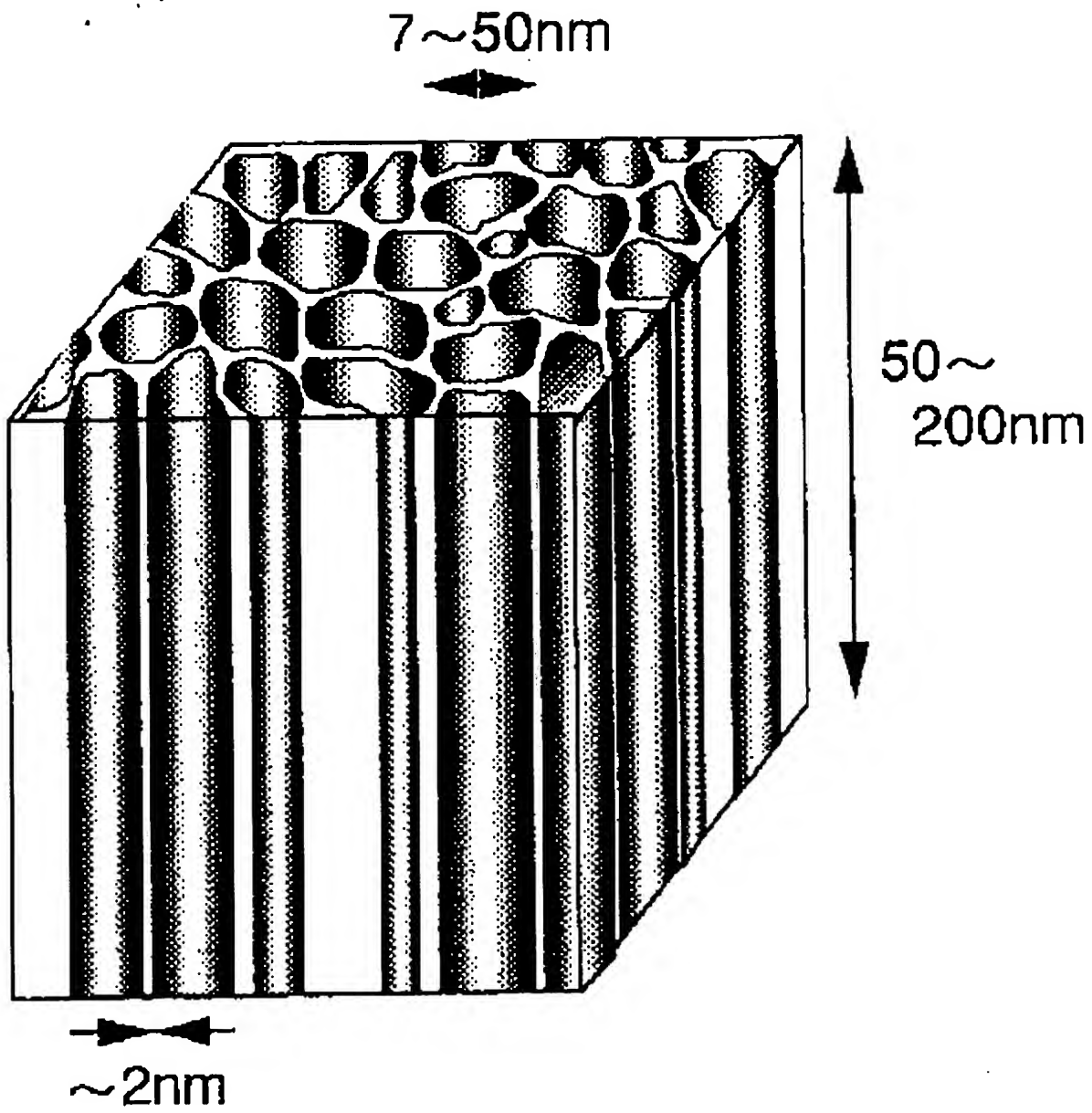
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